CONFERENCE ON DISARMAMENT

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Solid-phase extraction as a possible way of chemical warfare agents sampling for their analysis in laboratories under the Chemical Weapons Convention

The problem of sampling chemical warfare agents and transporting such samples to an analytical laboratory is difficult and not fully resolved yet. The sampling procedure and the form in which the sample is transported or stored may be decisive for the result of the analysis.

In contemporary analytical methods which allow identification of substances by comparison with standards or which allow their structures to be determined the quantity of sample may be very small. This is also true for quantitative analysis. Therefore small samples are sufficient for a full analysis of substances suspected to be chemical warfare agents.

To sample different toxic substances such as polyaromatic hydrocarbons and pesticides, solid-phase extraction (SPE) is very often used. To date it is not used for sampling chemical warfare agents. But it may be used in many cases for the purpose. Using this method, samples may be taken from installations, from water and from solutions in different organic solvents. Such solutions may be obtained after washing off some contaminated materials or by extraction of soil. SPE may also be used for the isolation of chemical warfare agents or their metabolites from biological matrices such as plasma or serum. The matrix frequently interferes with the determination of the analyte and SPE is a way of separating them.

The SPE method relies on adsorbing the substance to be analysed on adsorbent in a column; liquid chemical warfare agents directly and liquid and solid ones from solvent by an adsorbent. In this manner instead of transporting liquid or a large volume of solution we need only to transport a small column with adsorbed substance. The columns after closing firmly may be transported safely. Even after damage to the columns the adsorbed substance is desorbed very slowly and the chance of producing a harmful concentration of the substance in air is very small.

The adsorbed substance is eluted from the column using small amount of proper solvent receiving pure solution, much more concentrated in comparison with initial solution and good for analysis using different analytical methods.

Commercial columns filled with different adsorbents are available. The materials and equipment for SPE are produced by several firms.

J.T. Baker SPE system e.g. comprises polypropylene columns prepacked with high capacity sorbents contained between two polyethylene sinters. Glass columns with teflon sinters are also available. The sorbent choices comprise reverse phase, normal phase or ion exchange silica gel-based bonded phases. Columns are also available packed with normal phase adsorbents or size exclusion gel.

The volume of columns for extraction are 1, 3 or 6 ml. According to their capacity the weight of adsorbents in them is 100, 200, 500 or 1,000 mg.

The scheme of the SPE column is shown in figure 1.

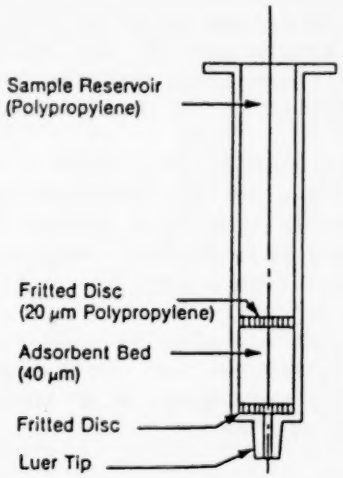


Fig. 1. Disposable extraction column.

Using the SPE columns it is possible to extract substances from sample solution volumes which range from a few hundred microlitres to several hundred millilitres.

SPE columns can be processed by vacuum, positive pressure or centrifugation. The most convenient is to process the columns by vacuum using a special system - figure 2.

SPE is a sample preparation technique based on the separation mechanisms of liquid chromatography. In SPE the solubility and functional group interactions of substance to be analysed, sorbent and solvent are optimized to effect retention or elution.

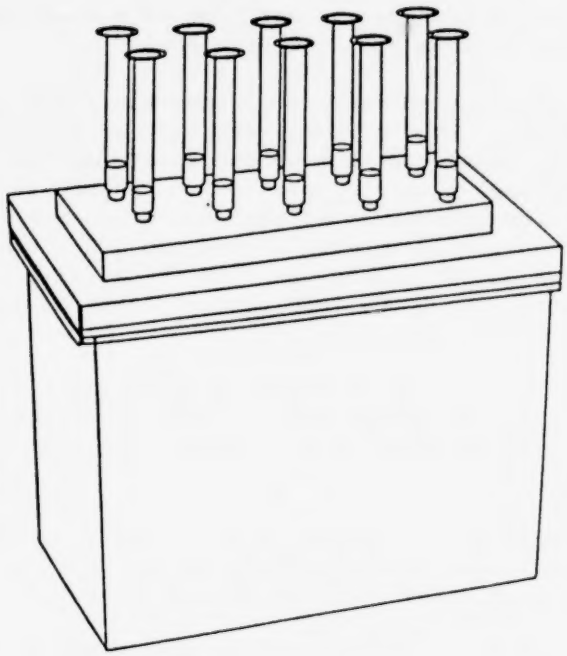


Fig. 2. Vacuum manifold extraction system.

When the analyst has a liquid substance to be analysed he is able to sorb it on the adsorbent at a place of sampling and to elute it in the laboratory. For a polar analyte a polar adsorbent should be used. For nonpolar substances to be analysed nonpolar adsorbents and solvents are recommended.

Having analytical samples as solutions sample cleanup and concentration are possible. When the analyst has a sample containing an analyte more polar than associated impurities, normal phase conditions should be selected. In this case the sample should be dissolved in a solvent (e.g. methylene chloride) less polar than the adsorbent (silica). Upon passing the solution through the column, the polar analyte is adsorbed by the silica; the relatively nonpolar impurities have greater affinity for the solvent and pass through the column. The polar analyte is then removed from the column by the addition of a more polar solvent which competes more effectively for the analyte than the silica itself. Thus, the polar analyte has actually been separated from the less polar impurities.

When the impurities are more polar than the analyte, a reversed phase system applies. The sample is dissolved in a polar medium and the solution is passed through a nonpolar adsorbent. The polar impurities remain in the solvent system and pass through the column. The less polar analyte is adsorbed by the low polarity adsorbent. Addition of a nonpolar solvent then elutes it thus separating it from polar impurities.

Reversed phase solid-phase extraction is convenient for concentrating organic substances in water. When a 75 ml reservoir is attached to 6 ml nonpolar octadecyl column connected to a vacuum manifold, the processing of a 500 ml aqueous sample becomes a simple operation. The entire 500 ml aqueous sample is drawn through the reservoir and the nonpolar organic trace components are retained on the adsorbent. Water and polar components pass through the column. Elution of the analyte with 500 μl of appropriate solvent provides a simple cleanup and a 1,000 fold concentration of the analyte in the eluate.

The above technique of trace enrichment is appropriate for field sampling of large volumes of water. The method can be simplified by the insertion of disposable columns in a vacuum manifold connected via a trap to a small portable pump.

For sampling chemical warfare agents normal phase chromatography with polar adsorbents and with polar bonded silicas and reversed phase chromatography with nonpolar bonded silicas are used.

Normal phase chromatography refers to a system in which the adsorbent is more polar than the mobile phase. Silica, alumina and activated magnesium silicate are used for SPE; silica is the most common. The polar surface of silica adsorbs slightly or moderately polar compounds dissolved in nonpolar or slightly polar organic solvents. Such analytes are eluted from the column with polar solvents. However, water soluble organics are too polar as they adhere so tightly to silica that elution by any solvent is impractical.

Using normal phase chromatography with polar bonded silicas compounds of moderate to strong polarity adsorb on them. The sample is dissolved in a solvent possessing as low polarity as possible; the analyte is eluted with a solvent of high polarity.

Reversed phase chromatography refers to any system in which the adsorbent is less polar than the mobile phase. Here nonpolar phenyl, octyl and actadecyl substituted siloxanes adsorb nonpolar or slightly polar analytes dissolved in polar solvents. These bonded phases are used for the analysis of trace organics in aqueous matrices in clinical and environmental analysis. The analytes are generally eluted from these sorbents with solvents of low polarity.

The examples of sorbents for SPE are shown in Table 1.

The scheme showing how the selection of an SPE system depends upon sample type is shown in Table 2.

Table 1. The examples of sorbents for solid-phase extraction

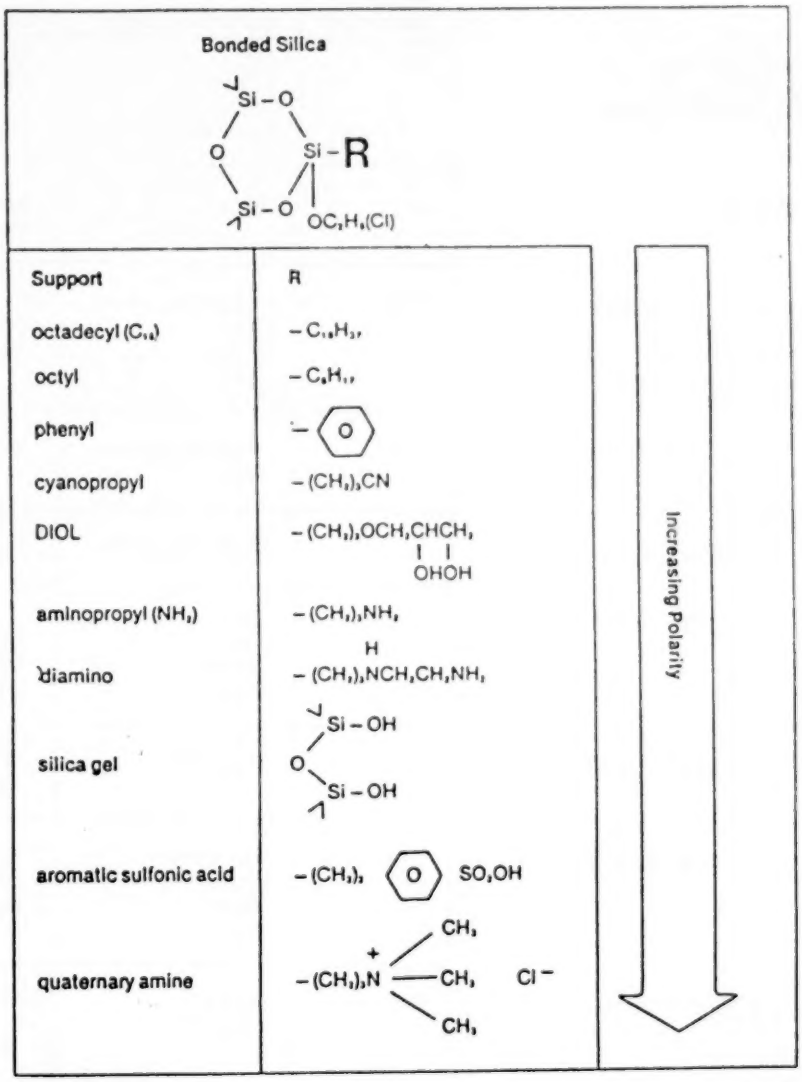
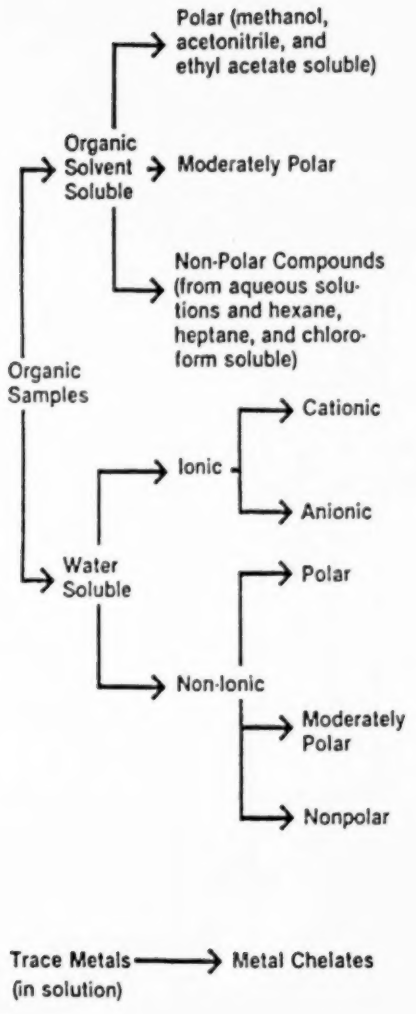


Table 2. The selection of solid-phase extraction system



Separation Mechanism[1]	Extraction Column[2]	Elution Solvent[3,4]
NPC	Diol Cyano Amino Diamino	Isopropanol Methanol
LSC	Silica Gel	Isopropanol Methanol
RPC	Octadecyl Octyl Phenyl Cyano	Hexane Chloroform Methanol
IEC	Aromatic Sulfonic Acid	Acid
IEC	Quaternary Amine	Base
NPC	Diol Cyano Amino Diamino	Isopropanol Methanol
LSC	Silica Gel	Isopropanol Methanol
RPC	Octadecyl Octyl Phenyl Cyano	Hexane Chloroform Methanol
IEC	Amino Diamino	Low pH Aqueous 1-8N HCl Strong Chelators (Thiourea)

[1]Separation Mechanisms
LSC: Liquid-Solid Chromatography (Adsorption)
NPC: Normal-Phase Chromatography (Bonded Phase Partition)
RPC: Reversed Phase Chromatography (Bonded Phase Partition)
IEC: Ion-Exchange Chromatography (Bonded Phase Ion-Exchange)
[2]Extraction columns listed in degree of increasing polarity
[3]Eluting solvents listed in degree of increasing polarity
[4]Selective elution can be performed by combining two or more miscible solvents to achieve various degrees of polarity

Solid-phase extraction is performed in four steps - figure 4.

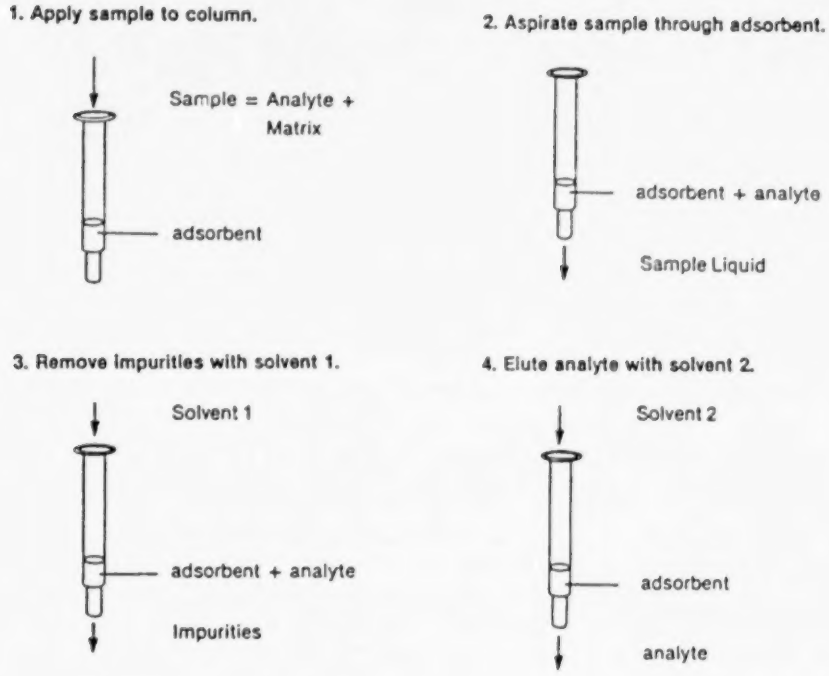


Fig. 4. Solid-phase extraction process

Ways of using SPE for collecting and preparing samples of chemical warfare agents are not well recorded. But it is possible to prepare procedures useful for sampling substances during inspections envisaged in the convention on chemical weapons.